Degradation of Impact Toughness due to Formation of R Phase in High Nitrogen 25Cr-7Ni-Mo Duplex Stainless Steels

Jie CUI, In-Sung PARK, Chang-Yong KANG¹⁾ and Kazuya MIYAHARA²⁾

Graduate School, Nagoya University, Nagoya 464-8603 Japan.
National University, Yong Dang-Dong, Nam-ku, Pusan, Korea.
Nagoya University, Nagoya 464-8603 Japan.

1) Department of Metallurgical Engineering, Pukyong
2) Department of Molecular Design and Engineering,

(Received on August 10, 2000; accepted in final form on November 2, 2000)

Influences of the formation behavior of the R phase on the hardness and the impact toughness were experimentally studied for high nitrogen duplex stainless steels containing 25 mass% of Cr, 7 mass% of Ni, 3 to 5 mass% of Mo, 0.14 to 0.27 mass% of N, and 0.02 mass% of C. The steels were solution heat treated at 1323 K for 3.6 ks, and then aged at 873 K for various times between 1.0 and 1.08×10^4 ks. For the aged steels, the hardness and the impact toughness were examined with a Vickers hardness test and a Charpy impact test, respectively, whereas the microstructure was observed by transmission electron microscopy as well as by optical microscopy. The experimental results indicate that thin and fine platelet precipitates of the R phase are formed along the {110} planes of body-centered cubic (b.c.c) ferrite (α phase) at early stages of the aging. The formation of the platelet precipitates of the R phase causes the brittle fracture of the α phase and thus the significant degradation of the impact toughness.

KEY WORDS: duplex stainless steel; nitrogen; R phase; molybdenum; impact toughness; aging treatment; precipitation; morphology.

1. Introduction

The impact toughness for high nitrogen Cr–Ni–Mo duplex stainless steels is known to be degraded during aging at temperatures around 900 K. Many investigators^{1–6)} proposed that such degradation of the impact toughness was caused by the precipitation of σ phase during aging. The relationship between the impact toughness and the microstructural change was experimentally studied by the present authors⁷⁾ using a commercial steel containing 24.7 mass% of Cr, 6.8 mass% of Ni, 2.8 mass% of Mo, 0.14 mass% of N and 0.017 mass% of C. The steel was aged at 873 K for various times and then metallographically observed by transmission electron microscope. According to the observation, however, the R phase is formed much earlier than the precipitation of the σ phase during the aging and the formation of the R phase results in remarkable degradation of the impact toughness at early stages of the aging. Here, the crystal system and space group of the R

phase are hexagonal and $R\bar{3}$, respectively, and its lattices parameters are $a=1.0903$ nm and $c=1.9342$ nm⁸⁾. The phase stability of the R phase increases with increasing Mo concentration in the steel.⁹⁾ In the present study, influences of Mo and N on the impact toughness were experimentally examined using high nitrogen 25Cr–7Ni–Mo steels aged at 873 K in a similar manner to a previous study.⁷⁾

2. Experimental

Two different high nitrogen Cr–Ni–Mo duplex stainless steels were newly prepared by vacuum induction melting in the present study. The chemical compositions of these steels as well as that of the steel in a previous study⁷⁾ are listed in **Table 1**. In this table, alloy 25Cr–7Ni is a commercial steel containing 2.8 mass% of Mo and 0.14 mass% of N utilized in a previous study, whereas alloy 25Cr–7Ni–N is a commercial steel containing 3.8 mass% of Mo and 0.27 mass% of N. On the other hand, alloy 25Cr–7Ni–Mo is a

Table 1. Chemical composition of steels in mass%.

Alloy	N	C	Cr	Ni	Mo	Si	Mn	P	S	W	Cu
25Cr-7Ni	0.143	0.017	24.66	6.82	2.79	0.48	0.85	0.025	0.001	0.28	0.46
25Cr-7Ni-N	0.270	0.020	25.00	7.00	3.80	0.30	0.40	0.010	0.010	--	--
25Cr-7Ni-Mo	0.170	0.020	24.99	7.00	4.97	0.51	0.85	0.024	0.002	--	0.01

Fig. 1. Optical micrographs for solution heat treatment at 1323 K for 3.6 ks: (a) alloy 25Cr-7Ni, and (b) alloy 25Cr-7Ni-N.

model steel with Mo and N concentrations of 5.0 and 0.17 mass%, respectively. The concentration of C is about 0.02 mass% for these steels. All the steels were hot rolled and then solution heat treated at 1323 K for 3.6 ks, followed by water quenching. After the solution heat treatment, the steels were aged at 873 K for various times between 1 and 1.08×10^4 ks.

On the aged steels, Vickers hardness tests were carried out at a load of 98 N, whereas Charpy impact tests were made at a temperature of 273 K using half-size V-notch specimens of JIS-Z2202-No.4 with a size of $5.0 \times 10.0 \times 55.0 \text{ mm}^3$. The microstructure was observed by transmission electron microscopy (TEM) and by optical microscopy.

3. Results and Discussion

Typical microstructures of the solution heat treated steels are shown in Fig. 1. Figures 1(a) and 1(b) indicate optical micrographs of alloys 25Cr-7Ni and 25Cr-7Ni-N, respectively. As can be seen in these figures, two-phase microstructures consisting of body-centered cubic (b.c.c) ferrite (α) and face-centered cubic (f.c.c) austenite (γ) are realized after the solution heat treatment. In these two-phase microstructures, the matrix and second phases are the α and γ phases, respectively. The volume fractions of the α and γ phases are almost the same in both alloys as shown in Figs. 1(a) and 1(b).

Figure 2 indicates the aging time dependencies of the Vickers hardness for alloys 25Cr-7Ni and 25Cr-7Ni-N at 873 K. Our previous results⁷⁾ show that, after an incubation time of about 30 ks, the Vickers hardness of alloy 25Cr-7Ni gradually increases with increasing aging time t and that this gradual increase is caused by the formation of σ phase. A significant increase in the Vickers hardness after $t = 3.6 \times 10^2$ ks is attributed to the formation of a large volume of bulky σ phase.⁷⁾ Alloy 25Cr-7Ni-N also shows a gradual increase in the Vickers hardness after an incubation time of about 50 ks and a large increase in the hardness after the aging for $t = 5 \times 10^3$ ks. This large increase in the hardness is retarded by about 10^4 ks comparing with that of alloy 25Cr-7Ni. This means that the high nitrogen content retards the formation of a large volume of the σ phase.

The aging time dependence of the Charpy impact value is shown in Fig. 3. Solid squares, circles and triangles in this figure indicate the results of alloys 25Cr-7Ni,⁷⁾ 25Cr-7Ni-N and 25Cr-7Ni-Mo, respectively. A significant loss of the impact toughness for alloy 25Cr-7Ni occurs after the aging for $t = 3.6$ ks. The previous results indicate that the

Fig. 2. The Vickers hardness versus the aging time at 873 K for alloys 25Cr-7Ni,⁷⁾ and 25Cr-7Ni-N.

Fig. 3. The Charpy impact value versus the aging time at 873 K for alloys 25Cr-7Ni,⁷⁾ 25Cr-7Ni-N, and 25Cr-7Ni-Mo.

aging stage for the significant loss of the impact toughness corresponds to the stage, where the R phase is formed but the σ phase is not yet formed.⁷⁾ Figure 3 also indicates that alloys 25Cr-7Ni-N and 25Cr-7Ni-Mo show a large decrease in the impact toughness after the aging for 18 and 10.8–36 ks, respectively.

Figures 4(a) and 4(b) indicate bright-filed (BF) and dark-filed (DF) images, respectively, for alloy 25Cr-7Ni-N aged at 873 K for $t = 18$ ks, whereas Fig. 4(c) shows a se-

lected-area diffraction (SAD) pattern taken from the precipitate phase in Figs. 4(a) and 4(b). In these BF and DF images, the matrix is the b.c.c.- α phase. Major spots of the SAD pattern in Fig. 4(c) are plotted as solid circles with indices in Fig. 4(d). The results in Figs. 4(c) and 4(d) indicate that the precipitate phase is R phase. The zone axis of the SAD pattern in Fig. 4(c) is $[3\bar{2}, 8, 7]_R$.

BF images of alloy 25Cr-7Ni-N aged at 873 K for $t=3.6, 10.8, 18$ and 36 ks are shown in Figs. 5(a), 5(b), 5(c) and 5(d), respectively. Figure 5(a) indicates that tiny dot like precipitates and coalesced particles are formed on dislocations and subboundaries as well as within grains in the α phase matrix after the aging for $t=3.6$ ks. Such a microstructure, however, has no effect on the impact toughness of the alloy. After the aging for $t=10.8$ ks, a small increase in the distribution density of these precipitates is observed, as shown in Fig. 5(b), and this causes a slight decrease in the impact toughness. For $t=18$ to 36 ks, a large number of platelet precipitates of the R phase are observed

Fig. 4. TEM observations of alloy 25Cr-7Ni-N aged at 873 K for 18 ks: (a) bright-field image, (b) dark-field image obtained using the $(218)_R$ spot, (c) selected-area diffraction (SAD) pattern of the R phase with the zone axis of $[3\bar{2}, 8, 7]_R$, and (d) schematic drawing of the SAD pattern in (c) with indices.

in Figs. 5(b) and 5(c), respectively. Accordingly, a large loss of the toughness is attributed to the formation of a large distribution density of the R phase platelets.

Typical BF and DF images of alloy 25Cr-7Ni-Mo aged at 873 K for $t=36$ ks are shown in Figs. 6(a) and 6(b), respectively. Also in these figures, the matrix and precipitate phases are the α and R phases, respectively. Figure 6(c) indicates SAD patterns for the α and R phase. In Fig. 6(d), major spots of the SAD pattern for the R phase are depicted as solid circles, whereas those of the SAD pattern for the α phase are drawn as smaller open circles. The zone axis of the SAD pattern for the α phase in Fig. 6(c) is $[001]_\alpha$, and the DF image in Fig. 6(b) is obtained using the $(444)_R$ spot of the SAD pattern for the R in Fig. 6(c).

Figure 7(a) shows a BF image of alloy 25Cr-7Ni-Mo aged at 873 K for 10.8 ks, whereas Fig. 7(b) indicates a

Fig. 6. TEM observations of alloy 25Cr-7Ni-Mo aged at 873 K for 36 ks: (a) bright-field image, (b) dark-field image obtained using the $(444)_R$ spot, (c) selected-area diffraction (SAD) patterns of the α and R phases with the zone axis of $[001]_\alpha$, and (d) schematic drawing of the SAD patterns in (c) with indices.

Fig. 5. Bright-field images of alloy 25Cr-7Ni-N aged at 873 K for times of (a) 3.6 ks, (b) 10.8 ks, (c) 18 ks, and (d) 36 ks.

Fig. 7. TEM observations of alloy 25Cr-7Ni-Mo aged at 873 K for 10.8 ks: (a) bright-field (BF) image, (b) selected-area diffraction pattern of the α phase with zone axis of $[001]_{\alpha}$ and (c) BF image obtained by tilting the specimen by an angle of 27.5° with the rotation axis parallel to the vertical direction of (a).

SAD pattern for the α phase. The zone axis of this SAD pattern is also $[001]_{\alpha}$. On the other hand, Fig. 7(c) shows a BF image obtained by tilting the specimen by an angle of 27.5° with the rotation axis parallel to the vertical direction of Fig. 7(a). As shown in Fig. 7(a), the R phase indicates the growth in the direction perpendicular to $[110]$ of the α phase matrix. These precipitates are considered to be noodle like or platelet precipitates. From Figs. 7(a) and 7(c), we can see that these precipitates are thin platelet precipitates formed on the $\{110\}$ planes of the matrix, because thin images of the precipitates observed in Fig. 7(a) become wide images in Fig. 7(c). The indeterminate form precipitates marked with A to C in Fig. 7(a) are considered to be thin platelet precipitates formed along other $\{110\}$ family planes (not parallel to the incident electron beam) of the matrix. A large distribution density of the thin and fine platelet precipitates of the R phase formed on the $\{110\}$ planes of the α phase matrix are considered to induce the brittle fracture of the α phase matrix along the $\{100\}_{\alpha}$ cleavage planes and to cause the significant loss of the toughness of the material.

4. Conclusions

The effects of the formation and morphology of the R phase on the impact toughness for high nitrogen 25Cr-7Ni-Mo duplex stainless steels aged at 873 K have been experi-

mentally observed. On the basis of the observations, the following conclusions have been drawn.

(1) Thin and fine platelet precipitates of the R phase cause the significant loss of the impact toughness.

(2) The platelet precipitates of the R phase are formed along the $\{110\}$ planes of the b.c.c.- α phase matrix at early stages of the aging. These precipitates may result in the brittle fracture of the α phase matrix and thus will induce the significant loss of the toughness of the steels.

REFERENCES

- 1) A. Hoshino, M. Kanao and K. Nakano *Tetsu-to-Hagané*, **63** (1977), 804.
- 2) E. Obata, K. Itoh and T. Iikubo: *Denki-Seiko*, **49** (1978), 242.
- 3) A. Hoshino, K. Nakano and M. Kanao, *Tetsu-to-Hagané*, **65** (1979), 70.
- 4) Y. Maehara, M. Koike, N. Fujino and T. Kuitake *Tetsu-to-Hagané*, **67** (1981), 577.
- 5) H. D. Solomon Proc. of Conf. on Duplex Stainless Steel, ed. by R. A. Lula, ASM, Metals Park, Ohio, (1982), 41.
- 6) S. C. Liu, H. Kuwano and Y. Hamaguchi *J. of Metals Inst. Japan*, **52** (1988), 917.
- 7) Y. Shimoi, J. Cui, C-Y. Kang and K. Miyahara: *ISIJ Int.*, **39** (1999), 191.
- 8) Y. Komura, W. G. Sly and D. P. Shoemaker: *Acta Crystallogr.*, **13** (1960), 575. (ASTM card: 26-425)
- 9) T. Kuroda, Y. Kikuchi, F. Matusda and K. Oe: *J. Soc. Mater. Sci., Jpn.*, **46** (1997), 592.